

ELECTRONICALLY CONDUCTIVE POLYMERS TYPE POLYPYRROLE AND POLYANILINE OBTAINED BY ELECTROPOLYMERIZATION ONTO ALUMINIUM SUBSTRATE

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Received March 20, 2008

Polypyrrole films and polyaniline films were electrodeposited at pure aluminium from an aqueous solution containing 0.1 M monomer (pyrrole or aniline) and 0.25 M oxalic acid.

The electropolymerization process was carried out by potentiodynamic method. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical properties of modified electrodes.

The results indicate that the mechanism of the redox process is complex and may be governed by the diffusion of the electrolyte. However, the aluminium substrate had a considerable effect on the electrochemical activity of the polypyrrole and polyaniline films and that, because in the presence of polymeric film, anodization of these modified electrodes resulted in formation of Al_2O_3 and polymeric layers simultaneously. This is consistent with a galvanic interaction between the polymer and the aluminium substrate, giving rise to oxidation of aluminium and reduction of the polymer. The increase of the cycles number led in all the cases to decrease of the anodic peaks height and of the anodic and cathodic current.

INTRODUCTION

In recent years, and particularly as a result of the developing semiconductor technology, the search for organic materials exhibiting electronic conductivity has become an active subject of study by both chemist and physicist.¹⁻³ There is a lot of literature concerning the synthesis and characterisation of conducting polymers. Electrochemical synthesis of conductive polymers allows preparation of layers of polymers of desired thickness; shape and dimensions generally are not possible by chemical methods. Thus far most promising conductive polymers have been those made from monomers of pyrrole, aniline, benzene, thiophene, acetylene. They have potential applications in electronic displays, as electrode materials in batteries, as molecular electronic circuit elements, as indicators of gasometers and biochemical analysis.

These polymers can be easily prepared electrolytically in organic or aqueous solutions.

Conductivity is usually in the semiconductor range. The conductivity of doped conducting polymers can be attributed to the delocalization of Π conjugated systems.

Polypyrrole does not require added dopants to be conductive. This polymer switches between a blank conductive form and a yellow nonconductive form by changing the applied potential on the underlying electrode.

The nature of the working electrode plays an important role in the electrodeposition of polypyrrole and polyaniline films. Thermodynamic study predicts that the metal will start to dissolve even before the electropolymerization potential of the monomer is reached.⁵ Thus, the right conditions are to be found where the passivation of the metal occurs without any hindrance to electropolymerization.⁶

In this paper, we have studied the formation of polypyrrole and polyaniline films on aluminium electrode using potentiodynamic method. The electrochemical properties of these polymeric films

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were studied by cyclic voltammetry and by electrochemical impedance spectroscopy.

EXPERIMENTAL

A model VoltaLab 40 potentiostat/galvanostat with EIS dynamic was used for the electrochemical polymerizations. Electropolymerization was done in three electrodes system.

A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrode respectively. The reference electrode was placed in a separate cell and was connected to the corrosion cell via a salt bridge, which ends as a Luggin capillary in the corrosion cell. This arrangement was used to reduce the ohmic resistance of the corrosion system. The working electrode was made of pure aluminium (99.9%). Samples with 0.64 cm^2 geometric surface area were used. Prior to experiments, the electrodes were polished with SiC emery paper down to #4000. After polishing, the electrodes were degreased in acetone, washed with Millipore water and then introduced into the measuring cell.

Polyaniline (PANI) and polypyrrole (PPY) films were electropolymerized onto an aluminium substrate by cyclic voltammetry with a scan rate of 20 mV/s . All the electropolymerization reactions were carried out in the scan range of -1000 to 3000 mV versus SCE. The obtained films were characterized by cyclic voltammetry, EIS measurements and metallographic microscopy.

The electropolymerization was carried out in 0.1 M monomer + 0.25 M oxalic acid electrolytic solutions. The electrochemical characteristics of the coatings were studied by cyclic voltammetry. The cycling solution was an aqueous solution of $0.5 \text{ M K}_2\text{SO}_4$. The working electrode potential was cycled on the potential range of -1000 mV up to 3000 mV with scan rate of 20 mV s^{-1} .

Impedance measurements were carried out using a VoltaLab 40 dynamic EIS, the instruments were controlled using a software program between 100 KHz and 10 mHz with an ac wave of $\pm 5 \text{ mV}$ (peak-to-peak) overload on a dc bias

potential and the impedance data were obtained at a rate of 10 points per decade change in frequency.

All tests have been performed at 25°C under atmospheric oxygen without agitation.

RESULTS AND DISCUSSION

In Fig. 1 are given the cyclic voltammograms of pyrrole polymerization in a synthesis solution of 0.25 M oxalic acid + 0.1 M pyrrole. The polymeric film was electrodeposited using potentiodynamic method. The electrode potential was scanned on the range of -1000 mV up to $+3000 \text{ mV}$ with a sweep rate of 20 mVs^{-1} for a period of 25 cycles.

Analyzing the cyclic voltammograms from Fig. 1, it can be observed that, at the first cycle on the anodic branch of the voltammogram appears an anodic peak, which is very high and wide. This anodic peak points out the anodic oxidation of pyrrole and the formation of polypyrrole film. The formation process of PPY film was illustrated by us in a previous paper⁷ and is in according to this mechanism, the electropolymerization reaction appears to involve two electrons per molecule of pyrrole (Py) monomer, and it proceeds through a radical coupling mechanism.⁸ During the formation, a stoichiometric amount of anions provided by the supporting electrolyte is incorporated into the polymer layer to neutralize the positive charge of the PPY chains. Therefore, the nature of the anions plays an important role in conferring the electrochemical properties of the PPY films.

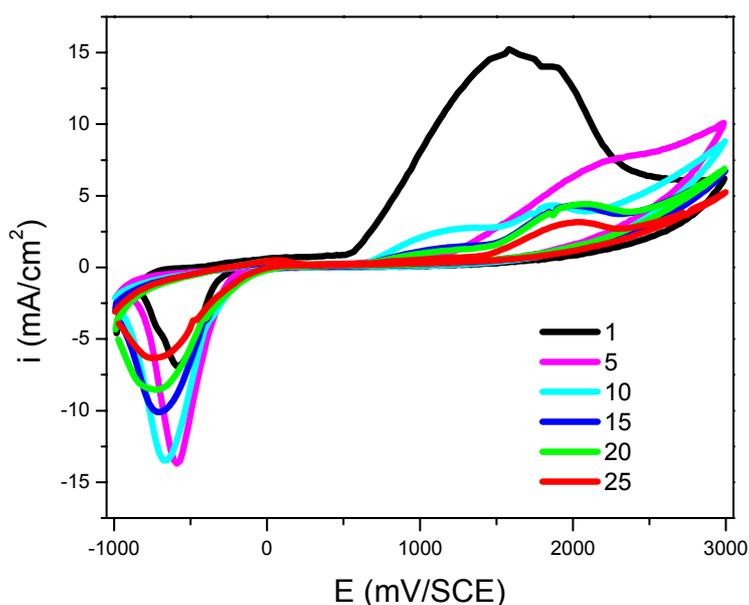


Fig. 1 – The cyclic voltammograms for the pyrrole electropolymerization.

At the reverse sweep electrode potential, on the cathodic branch of the voltammogram (for the first cycle) a reduction cathodic peak appears which is much lower than the anodic peak (see Fig. 1 and Table 1). The separation potential range (ΔE_p) between the anodic and cathodic peaks is wide enough and points out the fact that, at the electrode surface take place quasi-reversible processes. The value of ΔE_p is very high because the formation of PPY film led to the increase of ohmic resistance of the electrochemical system and consequently the charge transfer reactions are impeded and ΔE_p increases. After five cycles, the cyclic voltammogram obtained has a modified shape in comparison with the first cyclic voltammogram. In

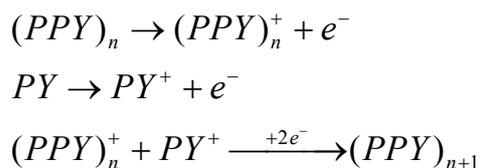
this case, at the anodic potential sweep appears an anodic oxidation peak, which has a lower height than in the case of the first cycle and it, is shifted to more anodic potential. On the cathodic branch of the cyclic voltammogram with number 5, the reduction cathodic peak appears in the same potential range, but in this case, it is more narrow and higher. Further, increasing number of cycles, it can be observed that, on the anodic branch appear two anodic oxidation peaks which have much lower currents densities and also, on the cathodic branch of the cyclic voltammograms appears a reduction cathodic peak. The height of this peak decreases with the increase of the cycles number (see Fig. 1 and Table 1).

Table 1

Kinetic parameters obtained from the cyclic voltammograms for pyrrole electropolymerization in 0.25 M oxalic acid aqueous solutions

No. cycle	i_{pa_1} (mA/cm ²)	E_{pa_1} (mV)	i_{pa_2} (mA/cm ²)	E_{pa_2} (mV)	i_{pc_1} (mA/cm ²)	E_{pc_1} (mV)	ΔE_{p_1} (mV)
1	16.38	1634	-	-	8.60	-578	2212
5	7.91	2235	-	-	14.51	-590	2825
10	2.70	1172	4.31	1815	13.49	-651	1823
15	1.31	1035	4.37	1896	10.08	-692	1727
20	1.18	1025	4.40	2032	8.53	-704	1729
25	0.66	1007	3.14	1970	6.29	-717	1724

We can explain this behaviour as follows: at the first cycle the electropolymerization reaction takes place and this reaction involves two electrons per molecule of monomer (Py) incorporated in the polymer, according to the following mechanism:



According to this mechanism, the electropolymerization of pyrrole is an anodic oxidation process and due to this processes the anodic current increases rapidly and an anodic oxidation peak (a) is obtained. At the reverse potential sweep a corresponding cathodic reduction peak (c) is obtained. The decrease of the anodic current peak height with the increase of the cycles number can be explained thus: at the anodic polarization of the aluminium electrode in synthesis solution, the formation of Al₂O₃ and PPY films proceeds simultaneously. At the first cycle the anodic oxidation of pyrrole to polypyrrole in according to the mechanism given before is predominant process. With the increase of the

cycles number the predominant process becomes the anodic oxidation of aluminium, with formation of Al₂O₃ film. The formation of Al₂O₃ can be explained as follows: the primary process in the electrochemical corrosion of aluminium is the formation of hexahydrated aluminium ion [Al(H₂O)₆]³⁺. In aqueous solutions of pH: 4-10,5 hexacoordinated aluminium ion forms different hydroxo complexes. Polynuclear complexes can be also formed depending on pH and aluminium ion concentration, consequently Al[O_x(OH)_y(H₂O)_z] is the idealized formula for the solid gel-like hydroxo complexes of undefined structure assigned to gelatinous alumina.⁹⁻¹¹ This gelatinous alumina transforms into different forms with different structures and finally, it can be obtained Al₂O₃ oxide film, which acts as an excellent barrier, inhibiting the charge transfer reactions. Hence, the formation of Al₂O₃ film inhibits the electrochemical polypyrrole formation and thus, we can explain the decreasing of the anodic oxidation current once with the increase of the cycles number. The apparition of the two anodic oxidation peaks together with the increase of the cycles number can be explained by oxidation of the hydroxocomplexes to Al₂O₃ and also, by oxidation of pyrrole with formation of polypyrrole film. The

two films interact one with the other and it can be considered that, the bilayer film was obtained consisting of a barrier-type Al_2O_3 and an electronically conducting PPY film. The formation of Al_2O_3 layer proceeds two interfaces, the first at the aluminium/ Al_2O_3 layer and the second at the Al_2O_3 layer/PPY film. It is assumed that, the species are continuously generated at metal/oxide interface. Then, they migrate through growing Al_2O_3 layer toward the solution under high electric field, while oxide ions O^{2-} migrate toward the aluminium electrode.¹² At the interface of Al_2O_3 layer/PPY film, the Al^{3+} encounters water species to form Al_2O_3 film. This way, it can be explained also the decreasing height of the reduction cathodic peaks once with the increase of the cycles number (see Fig. 1 and Table 1).

Further, were carried out the EIS measurements on the PPY/Al modified electrode in 0.5 M K_2SO_4 solution after a number of 5 cycles.

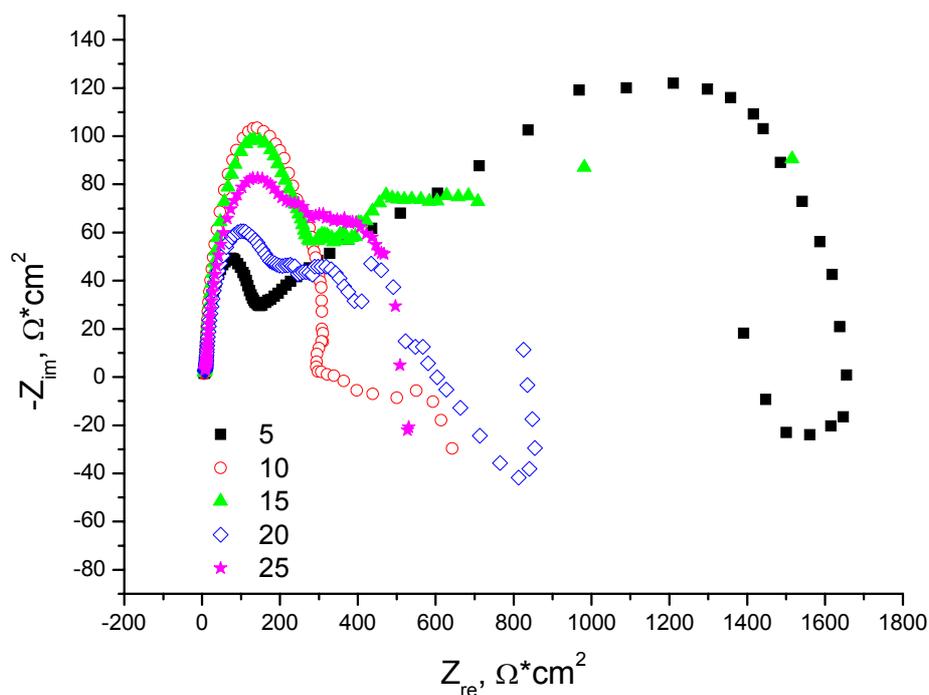


Fig. 2 – Nyquist diagrams for PPY/Al modified electrode in 0.5 M K_2SO_4 solutions in relation to the number of electrodeposition cycles.

The Nyquist diagrams for cycles 10 and 15 have the highest capacitive loops in the high frequencies range and this fact can be explained by formation of Al_2O_3 layer which is well formatted after this cycling period and acts as a barrier for the charge transfer reactions. On these diagrams in the medium frequencies range appears a second capacitive loop which pointed out the two interfaces formation as follows: an interface

In Fig. 2 are given the Nyquist diagrams for these measurements. Analyzing the Nyquist diagram for the cycle number five, it can be observed that, at the high frequencies, a capacitive loop very well defined is obtained and that is followed by a diffusive branch at the medium frequencies and an inductive loop at low frequencies. The capacitive loop pointed out the PPY film formation and the incipient formation of Al_2O_3 layer. The diffusive branch pointed out that, in this frequencies range take place the diffusive processes, this means that the PPY and Al_2O_3 are not enough compact and adherent films. The inductive loop indicates that in the low frequencies range takes place the adsorption of some ionic species followed by relaxation phenomena.

between the base metal (Al) and Al_2O_3 formed layer and the second interface between Al_2O_3 formed layer and PPY polymerized film. After these capacitive loops, in the low and very low frequencies two inductive regions are obtained. These inductive regions pointed out the adsorption of the active species on the electrode surface followed by the relaxation phenomena on the PPY film surface.

In the case of Nyquist diagram for the cycle number 20, the first capacitive loop which appears in the high frequencies range decreases in comparison with Nyquist diagrams for cycles 10 and 15. We presume that in this case, after a prolonged anodic oxidation the PPY film becomes loose and porous and the polarization resistance decreases. The second capacitive loop from the medium frequencies range decreases too and then at the low frequencies an inductive region is obtained. Finally, at the very low frequency range a pure capacitive behaviour is obtained (a linear branch parallel with $-Z_{im}$ axis).

This fact pointed out that, in this case, after a prolonged anodic oxidation, the Al_2O_3 oxide layer is very well formed and it is very compact and adherent.

The corresponding Bode diagrams are in good concordance with the Nyquist diagrams (see Fig.

3a and 3b). As we can see from the Bode diagram, at the high frequencies on the phase angle versus log frequency curve, there appears a maximum very well definite that corresponds to phase angle of 65° , which indicates a capacitive behaviour of the PPY/Al modified electrode in the given solution and after a cycling period of 10-15 cycles. For the cycles 20, 25 and 5, the phase angle has a value of 50° and this fact indicates a capacitive behaviour with diffusive tendency. At the low frequencies, on the phase angle versus log frequency curve appears a second maximum, much lower than the first maximum, which was obtained at the high and very high frequencies. The second maximum indicates an inductive behaviour of the modified electrode type PPY/Al in the given solution and after different cycling periods.

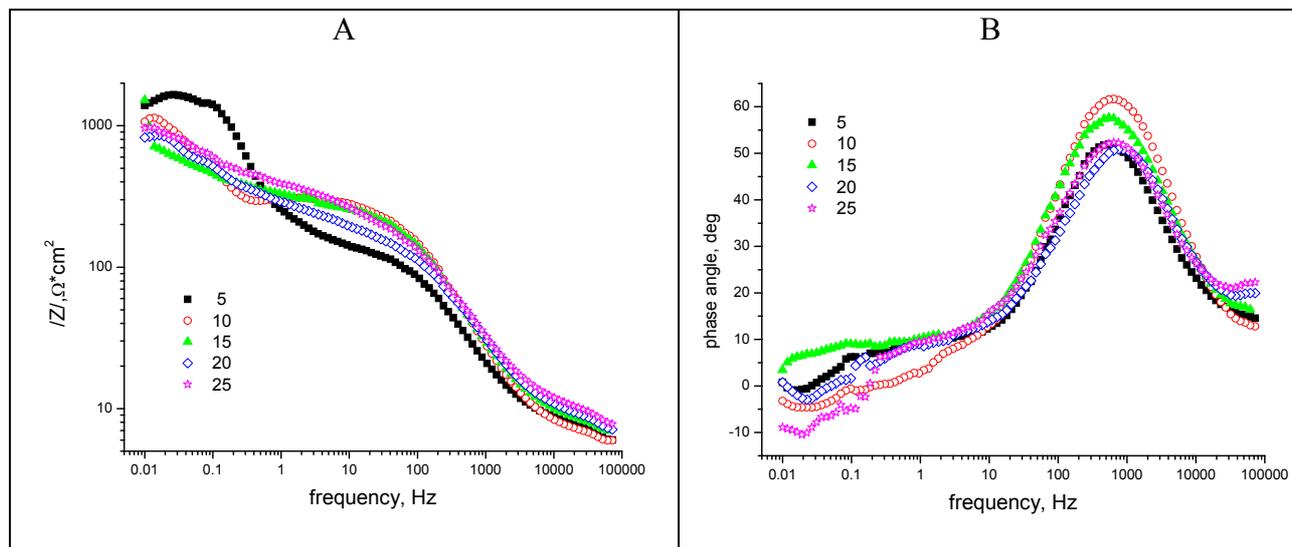
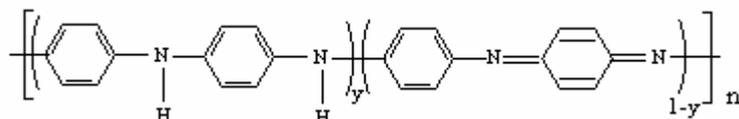


Fig. 3 – Bode diagrams for PPY/Al modified electrode in 0.5 M K_2SO_4 solutions in relation to the number of electrodeposition cycles.

Also, we analyzed by metallographic microscopy the modified electrode PPY/Al surface and in Fig. 4 are given a micrographic image. Analysing this micrography, it can be observed very well the electrodeposited polypyrrole layer and its characteristic structure like as cauliflower. This image proves once again the formation of the PPY layer on the aluminium substrate by cyclic voltammetry and its characteristic structure. Further, we studied the obtainment of the polyaniline films on the aluminium substrate by using cyclic voltammetry.

In Fig. 5 are given the cyclic voltammograms of aniline polymerization in a synthesis solution of 0.25 M oxalic acid + 0.1M aniline. Analyzing the

cyclic voltammograms from Fig. 5, it can be observed that, at the first cycle on the anodic branch of the voltammogram appears two anodic oxidation peaks which point out the anodic oxidation of aniline and the formation of polyaniline (PANI) film. It is well known that, polyaniline can exist in three different oxidation states such as leucoemeraldine (fully reduced form), emeraldine form (partially oxidized form) and pernigraniline (fully oxidized form). A very important characteristic of polyaniline consists in the fact that its structural units contain two different entities with different ponderables. Taking into account this property we can write thus:



when $y = 1$, we have leucoemeraldine base, when $y = 0$ we obtained pernigraniline base and when $y = 0.5$ an intermediate state between leucoemeraldine

and pernigraniline is obtained which is called emeraldine base.

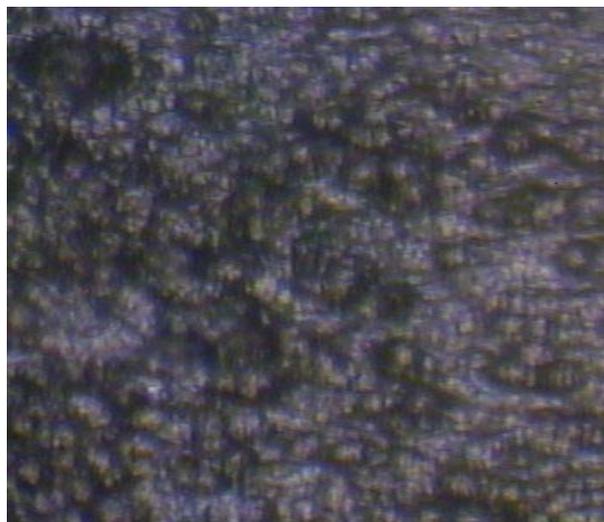


Fig. 4 – Micrographic image of PPY film electrodeposited on aluminium surface after 25 cycles.

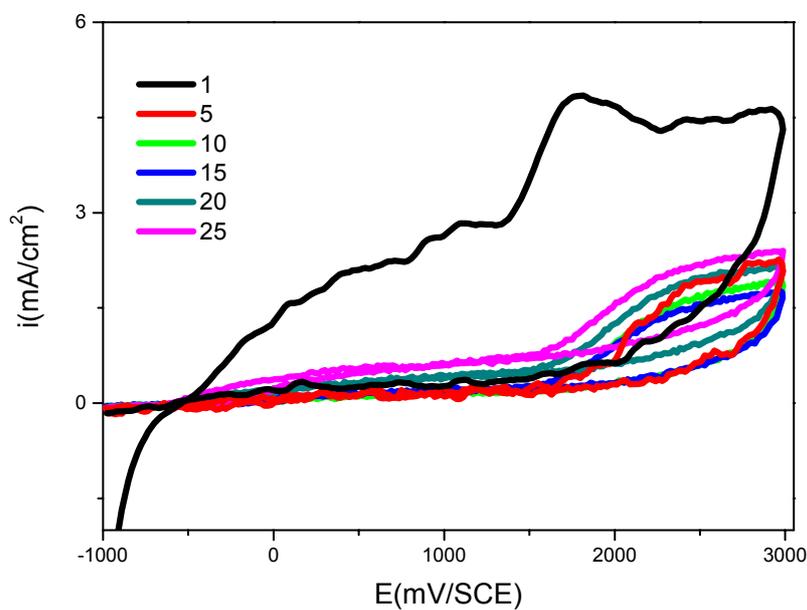


Fig. 5 – The cyclic voltammograms for the aniline polymerization.

These forms of polyaniline are dependent on the applied potential. At the increasing anodic potential sweep the oxidation forms of polyaniline are obtained and on the anodic branch of the cyclic voltammogram appear the oxidation peaks.

The formation process of PANI film was illustrated by us in a previous paper.¹³

At the reverse potential sweep, no cathodic reduction peak appears up to -1000 mV, but it can be observed that, the cathodic current begins to increase at a potential value of -650 mV (see Fig. 5). The increase of the number of cycles led in all the cases to decrease of the height of the anodic peaks and also, to decrease of the anodic and cathodic current (see Fig. 5 and Table 2).

Table 2

Kinetic parameters obtained from the cyclic voltammograms for aniline electropolymerisation in 0.25 M oxalic acid aqueous solutions

No. cycle	i_{pa_1} (mA/cm ²)	E_{pa_1} (mV)	i_{pa_2} (mA/cm ²)	E_{pa_2} (mV)
1	2.83	1091	7.83	1777
5	1.27	2141	1.92	2484
10	-	-	1.72	2561
15	-	-	1.83	2512
20	-	-	1.98	2508
25	-	-	2.13	2424

We can see that, after five cycles on the anodic branch of voltammogram appears only one anodic oxidation peak and its height is much lower than in the case of the first cycle. This decrease of the anodic peak height and of the anodic and cathodic current once with the increase of the cycles number is due to the formation of the Al₂O₃ passive layer

which behaves as a barrier for charge transfer reaction (as we explained above in the paper).

The EIS measurements are presented by Nyquist and Bode diagrams. In Fig. 6 are given the Nyquist diagrams for PANI/Al modified electrode in 0.5 M K₂SO₄ solutions in relation to the number of electrodeposition cycles.

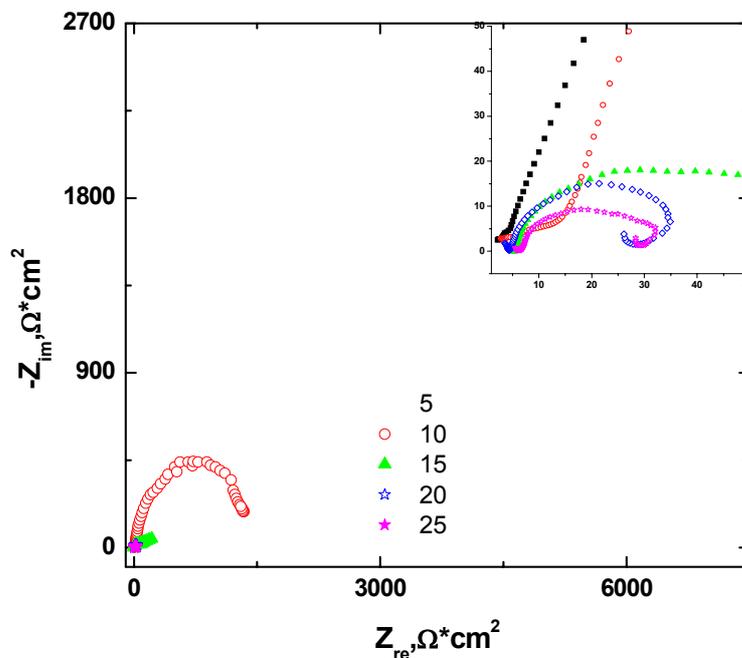


Fig. 6 – Nyquist diagrams for PANI/Al modified electrode in 0.5 M K₂SO₄ solutions in relation to the number of electrodeposition cycles.

Analyzing these diagrams from Fig. 6, it can be observed that, after five of electrodeposition cycles, on the Nyquist diagram appears a large and high capacitive loop in the high frequencies range and this is followed by the linear branch which has a very low slope ($\ll 1$) and this means that in this low frequencies range the PANI/Al modified electrode has a diffusive behaviour with inductive tendency. Together with the increase of the electrodeposition cycles, the capacitive loop height decrease and the inductive region increases (see Fig. 6). This behaviour can be explained considering

that, after the first five cycles of electrodeposition, the PANI film is very compact and adherent and then, with the increasing of the cycles number this becomes loose and porous and consequently the polarization resistance decreases as we can see very well in Fig. 6 and Fig. 7. Fig. 7 shows the Bode diagrams and these are in according to the Nyquist diagrams. From Fig. 7, we can see that, for the cycle number 5, the phase angle has a value of 70° and that indicates a capacitive behaviour at the high frequencies.

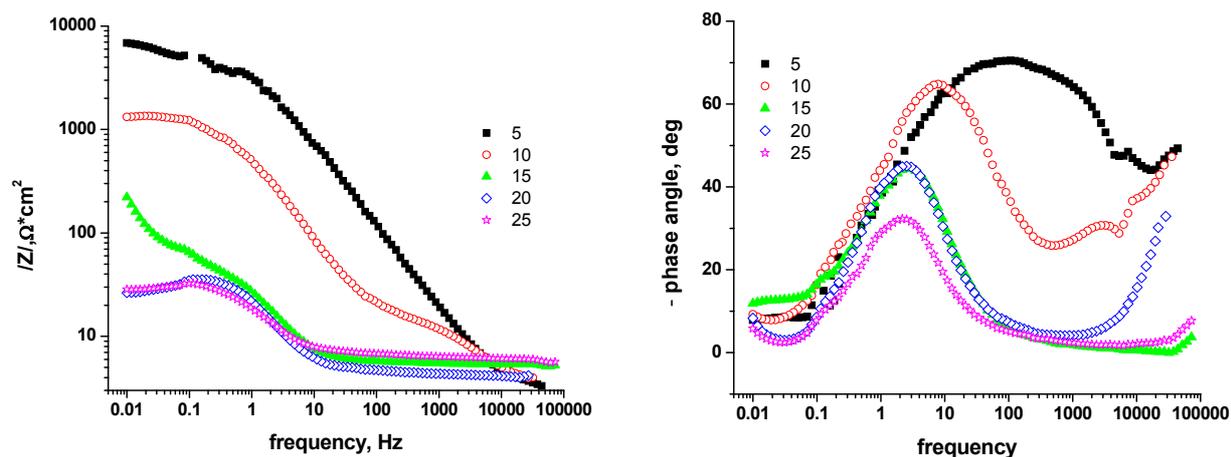


Fig. 7 – Bode diagrams for PANI/Al modified electrode in 0.5 M K_2SO_4 solutions in relation to the number of the electrodeposition cycles.

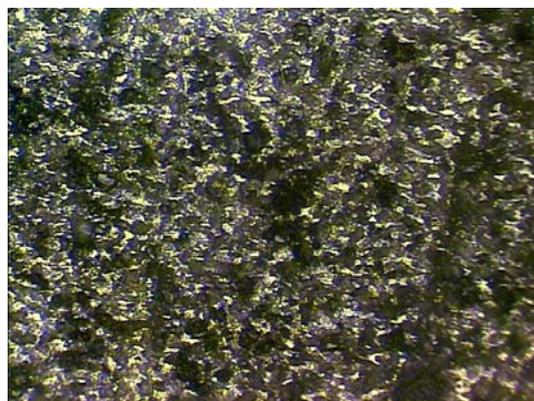
The same behaviour can be observed for the PANI/Al modified electrode obtained after 10 electropolymerized cycles, while for the electropolymerized cycles with numbers 15, 20 and 25 the phase angles, have values lower than 40° that means a diffusive behaviour with inductive tendency which is according to the results obtained by cyclic voltammetry.

Also, we analyzed by metallographic microscopy the modified electrode PANI/Al surface and in Fig. 8 are given the micrographic images. Analyzing these micrographies, it can be observed very well the

electrodeposited polyaniline (PANI) layer and its characteristic morphological structure, which is composed from long chances of polymer uniform distributed on the whole aluminium surface. This fact confirms once again the oxidation of aniline at the anodic polarization and electrodeposition of the polyaniline film on the aluminium substrate in concordance with voltammetric and EIS obtained results.



a) PANI/Al +200x



b) PANI/Al + 400x

Fig. 8 – Micrography images of PANI film electrodeposited on aluminium surface after 25 cycles.

CONCLUSIONS

The electropolymerization of pyrrole is an anodic oxidation process, which involves two electrons per molecule of monomer incorporated in the polymer chain.

The formation of Al_2O_3 film inhibits the electrochemical polypyrrole formation and thus the decrease of the anodic oxidation current takes place.

After a prolonged anodic oxidation the PPY film becomes loose and porous and the polarization resistance decreases.

The increase of the cycles number led in all the cases to decrease of the anodic peak height and of the average value of the anodic and cathodic current.

The electropolymerization of aniline is an anodic oxidation process, which leads to formation of polyaniline in three different oxidation states such

as, leucoemeraldine (fully reduced form), emeraldine form (partially oxidized form) and pernigraniline (fully oxidized form).

For PANI/Al modified electrodes the increase of the number of polymerization cycles led in all the cases to decrease of the anodic peak height and to decrease of the anodic and cathodic current and in general of the average of the anodic and cathodic current.

The micrographic images pointed out the morphological structure of polypyrrole and polyaniline films and confirmed the electropolymerization of monomers at the anodic potential sweep.

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